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"CENTER FOR HIGH SPEED GAS DYNAMICS"

Final Technical Report

Grant # NCC1 131

To:

**NASA Langley Research Center
Hampton, Virginia 23681-0001
Attn: Joseph S. Murray/Grants Officer**

Prepared by:

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**(NASA-CR-199124) CENTER FOR HIGH
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Section I: Administrative Review

During 1987, and the early months of 1988, there were a series of discussions between members of ICASE, NASA-Langley, and Princeton University's MAE Department. These discussions led to the first Princeton proposal in May, 1988, on an "Initiation of a Program of Research on High-Speed Gas Dynamics." This first proposal was quickly replaced by a second proposal to set up a "Center for High-Speed Gas Dynamics," with three major partners; ICASE, NASA-Langley, and Princeton University's MAE Department. The original proposal for 16 months was changed to a proposal for June 1 to October 1, 1988 and, with the withdrawal of ICASE from the formal program, resulted in the first contract for \$125,000 between NASA-Langley, Hypersonic Technology Office, and Princeton University's MAE Department. This original effort was headed by Douglas Dwoyer of NASA, and Seymour Bogdonoff of Princeton University. Professor Bogdonoff was named the Director of the "Center."

The continuation of this original contract was requested in September of 1989, and an arrangement covering the period of October 1, 1988 to October 1, 1989, for \$200,000 was approved.

Discussions in late 1989 resulted in the continuation and an additional task, which included some European involvement, for a total commitment of \$550,000. The program ended September 30, 1990.

Section II: Brief Review of Technical Efforts

A) Introduction:

For some years, individuals in the three organizations (NASA-Langley's Hypersonic Technology Office, ICASE, and Princeton University's Department of Mechanical Aerospace Engineering) had close contact on many problems of mutual interest. The complementing talents, experience, and facilities, made it clear that a more formal arrangement, focused on specific areas of mutual interest, could provide a much enhanced program through intellectual stimulation and coordinated research planning, implementation, and evaluation. The discussions in the early spring of 1988 developed a proposed framework and goals for a "Center for High-Speed Gas Dynamics." The "Center" was planned to be headquartered at Princeton, and would consist of selected staff from the Hypersonic Technology Office at NASA Langley, ICASE, and the Mechanical Engineering Department of Princeton University. The "Center" was planned to provide a framework for cooperatively studying problems of high-speed gas dynamics relevant to the design of future high-speed aerospace vehicles. The studies to be carried out by the center, theoretical, computational, and experimental, would be developed and implemented by a coordinated, broad front attack on selected problems. It was believed that a coordinated program consisting of frequent individual meetings, group meetings, seminars, work shops, planning sessions and reviews, would considerably enhance the three organizations' known ability to make significant contribution to the high-speed arena.

Interchange of staff in all three organizations was an integral part of the original planning. In the initial discussions, it was planned that, as the "Center" progressed through interactions and involvement in problems and discussions, special projects - formulated by the "Center," and individual researchers - would be submitted to NASA, other government agencies, and foundations, for individual support. During the period of

this contract, the primary research funding was through ongoing contracts, with the “Center” providing supplements to focus on hypersonic topics.

B) Goals:

The goals of the proposed “Center” was to provide; 1) a frame work for cooperatively studying problems of high-speed gas dynamics relevant to high-speed aerospace vehicles, including aerodynamics, propulsion, propulsion integration, transition and turbulence, mixing, combustion, and real gas effects. These problems of mutual interest would be attacked theoretically, computationally and experimentally. 2) Princeton University’s staff and students the opportunity to interact closely with a major national center for hypersonic research, with extensive staff and facilities, and 3) the NASA-Langley Hypersonic Technology Office and ICASE an opportunity to expand their contacts with the resources of the Mechanical Aerospace Engineering Department of Princeton University, the faculty, staff, students, and facilities.

C) Technical Program:

The initial efforts of the Center were primarily focused on supersonic mixing and combustion and a frame work of needs for hypersonics vehicles that consisted of the following six elements: 1) Exploratory experimental studies of H_2-O_2 reaction induction times. 2) Support and involvement in an “International work shop on the Physics of Compressible Turbulent Mixing.” 3) The planning and implementation of a supersonic combustion work shop. 4) Involvement in the ICASE summer activity on mathematical-computational techniques to study shock amplification of instability waves and turbulence. 5) An effort on the computational singular perturbation models for H_2-O_2 reactions. 6) A coordinated Princeton University, NASA-Langley HTO, and ICASE Program for investigating a) compressible shear layer stability (reacting and nonreacting), b) secondary

instability mechanisms, c) the role of eddy shocklets, d) details of experimental programs, and e) the design of appropriate supersonic combustion studies.

D) Brief Review of First Year

In the final arrangement of the first year of activity, ICASE withdrew as a formal partner, although they continued to be involved in many of the activities. The "Center" at Princeton had five of the faculty deeply involved in a full range of activities and interactions envisioned in the original formulation of the center. Although much was accomplished, there was not the level of integration at Princeton and between Princeton and NASA-HTO that had been hoped for in the original discussions. The lack of progress in this area seemed to stem, not from a lack of interest, but a series of unplanned critical activities (both at Princeton and at NASA) which limited the availability of key personnel at critical points in the program.

The "Center" partially supported and was deeply involved in the "International work shop on the Physics of Turbulent Compressible Mixing," held on October 24-27 1988 at Princeton, Reference 1. The spring lecture series, held by the "Center" at Princeton, was very well received and attended, and a series of summer lectures under the auspices of the center were held at Princeton in July, Appendix 1. The faculty made multiple visits to NASA and to ICASE, involving technical discussions and the planning for a combustion work shop.

E) Brief Review of Second Year:

For the reasons noted above, based on experience with the first year and financial restrictions, a somewhat limited second year activity (about 1/2 the original plan) was continued. The lecture series and work shops which had been planned took place with considerable success, Appendix 1. Professor Claudio Bruno of Italy spent a month at

Princeton in the Fall, and had discussions with a wide group (Trip report, Appendix 2). Professors Glassman, Orszag, Jameson, Lam, and Bogdonoff, all made significant contributions and had many interactions with NASA's staff. All technical results have been discussed and transmitted, where appropriate, to NASA's staff, Reference 2, Appendix 3. Arrangements for interchange of personnel was not successfully completed due to commitments and funding limitations. Professor Garry Brown, who became the new Chair of the Department of Mechanical and Aerospace Engineering in June, 1990, continued discussions with NASA-Langley Hypersonic Technology Office. In the fall of 1990, it was decided not to continue the activities of the "Center" per se, but to revert again, to the individual proposal activities of the faculty.

The program ended with Princeton's faculty, staff, and students much more aware of and involved in problems of hypersonic flight.

References:

- 1) Workshop on "Physics of Compressible Turbulent Mixing"
- 2) "Revised" Proposal for continuation of "Center." Bogdonoff & Lam, Jan. 1990

Appendices:

- 1) Lecture Series
- 2) Bruno - Trip Report
- 3) Glassman Report

Reference 1:

International Workshop on the Physics of Compressible Turbulent Mixing

Princeton University, Princeton, New Jersey

October 24-27, 1988

Sponsors:

DOE: Lawrence Livermore National Laboratory

Los Alamos National Laboratory

DOD: Army Research Office, Engineering Sciences Branch

Office of Naval Research, Fluid Mechanics Program, Mechanics Branch

National Science Foundation

Fluid Dynamics & Hydraulics Branch

Combustion Sciences Branch, Engineering Division

Princeton University

Center for High Speed Gas Dynamics

Proceedings:

Publication of lectures and informative texts on poster presentations and a general summary of all of the presentations and discussions were published in a bound proceedings available approximately three months following the workshop. Publications appeared as part of the Springer-Verlag, New York, Inc.'s series: *Lecture Notes in Engineering*.

Reference 2:

“Revised” Proposal for continuation of “Center”. Bogdonoff and Lam, Jan. 1990

"REVISED"
PROPOSAL FOR CONTINUATION OF
"Center for High Speed Gas Dynamics"
GRANT NCC1-131

October 1, 1989 thru October 1, 1990

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January 1990

1. Introduction

The present proposal is a revision of a proposal dated September 1989 on a continuation of efforts started under Grant NCC1-131. During the past year, the "Center for High Speed Gas Dynamics" has explored, through all five of the current faculty involved, the full range of possible activities and interactions envisioned in the original formulation of the Center. Although much has been accomplished, there has not yet been the level of integration at Princeton and between Princeton and NASA that was hoped for in earlier discussions. The lack of great progress in this area seems to stem not from a lack of interest, but a series of unplanned activities (both at Princeton and at NASA) which has limited the availability of key personnel at critical times. Some of the proposed plans which follow focus on this problem.

In the following sections, the activities of the past year are briefly outlined, and the tentative plans for the present year are described. This is followed by a minimum budget for the year October 1, 1989 to October 1, 1990.

2. Brief Summary of Center Activity October 1, 1988 to October 1, 1989

1) The Center partially supported the "International Workshop on the Physics of Turbulent Compressible Mixing," on October 24-27, 1988, which was held at Princeton.

2) A spring lecture series was held under the auspices of the Center at Princeton during March, April and May, 1989. For several of these lecture series, NASA personnel came to Princeton. The series consisted of the following lecturers:

Richard Neumann, Wright Field Flight Dynamics Lab, March 27-29, 1989
Robert Cattolica, Sandia National Labs, April 10-12, 1989
Donald Baganoff, Stanford University, May 1-2, 1989
Seymour Bogdonoff, Princeton University, May 9, 1989

Sin-I Cheng, Princeton University, May 16, 1989

3) A summer lecture under the auspices of the Center was held at Princeton in July:

Robert Bilger, University of Sydney, July 17, 1989.

4) A series of visits were made by Princeton personnel to NASA-Langley and Headquarters regarding technical discussions and interchanges. Professor Bogdonoff made six trips to Langley and one trip to Headquarters. Professor Glassman and Dr. Brezinsky made one trip to Langley. These trips were all specifically concerned with Center activities. In addition to these visits, Professor Orszag made several visits to Dr. Hussaini regarding his compressible turbulence work. Professor Lam made two visits and gave lectures regarding his work on computational singular perturbation methods. Professor Bogdonoff made several visits in connection with other activities at Langley. Professor Glassman and Dr. Brezinsky interacted with Dr. Hussaini with regards to planning for a combustion seminar to be held this fall.

3. Summary of Research Activities and Tentative Plans for the Present Year

Several major commitments have already been made for the fall period. Professor Dean Chapman gave a lecture series on October 23 and 24. Dr. Ken Stetson of Wright-Patterson AFB gave a lecture series on November 13 and 15. Professor Claudio Bruno, formally at Milan, Italy and now at the University of Rome, spent four weeks at Princeton starting the end of October. Dr. Bruno is primarily concerned with the surface catalytic effect of combined fluid mechanics and chemistry. Besides interacting closely with the group at Princeton, he also worked closely with Prof. Eric Jumper, University of Notre Dame, Alex Harris of Bell Laboratory, Prof. Graham Candler of North Carolina

State University, Prof. Steve Bernasek of Frick Laboratory at Princeton, Prof. Sigurd Wagner of Electric Engineering at Princeton, Dr. Carl Scott of NASA-Johnson, David Stewart of NASA-Ames, and Jim Carter at UTRC (United Technologies, NASP Propulsion). This wide-ranging set of discussions provided a major focus for the Princeton group during his stay. There are tentative plans, funding permitting, to have him return for two months during the summer of 1990. Discussions with NASA personnel have explored the possibility of having a NASA employee at Princeton during the fall term and the possibility of having several visitors for periods of several days to several weeks, funding permitting.

Professor Glassman and his group have been working on fundamental problems of hydrogen oxygen combustion. In particular, they have concentrated on induction times of such systems. They have completed the first of their studies and are preparing Technical Note #1 for submission to the NASA-Langley Group. Some of the new understanding flowing from this work seems to strongly support the possible use of pyrophoric metals to aid supersonic mixing and reduce the induction period substantially. The work also indicates a significant effect on recombination of dissociated species in nozzle expansion flows. Continuation of this work is a major thrust during the present period. Continued experimental work at Princeton, and a much stronger interaction with the Langley group, should considerably strengthen this activity.

Professor Orszag concentrated on two efforts for the Center. One was the International Symposium on the Physics of Compressible Turbulent Mixing held in Princeton on October 24-27, 1988. This International Symposium was very successful, with many new results and exciting discoveries reported. The

major research activity was the work of Prof. Kida on compressible turbulence. His work seems to indicate that turbulence near Mach number of one showed a considerable difference in structures than the earlier work on incompressible turbulence. Kida also noted that regions of large entropy production in turbulence occurs immediately behind shock waves, and that there are significant correlations between density gradients and vorticity in turbulence passing through shock waves. Professor Kida will continue this work and is preparing a number of research publications before he completes his activity at the Center the end of April, to return to Japan.

Professor Jameson has a major activity in the examination of computational techniques for hypersonics and is currently involved in several thrusts of importance to the Center. His algorithm development and efforts to add viscosity and chemistry to his earlier Euler work is of key importance in the high speed area. One of his students is working with Professor Bogdonoff in an attempt to provide another series of computations to compare with the experimentally studied complex shock wave boundary layer interactions, currently only computable by full Navier-Stokes solutions. The comparison of the different techniques should provide a very vital new understanding of the key parameters that are required in the computation of such flows.

Professor S. H. Lam has made significant progress in the continuing development of his computational singular perturbation (CSP) technique. The original concept, developed in 1985, has now been considerably expanded. The present work is to extend the technique to problems of practical interest to gain better physical understanding and insights of the importance of chemical kinetics to high speed fluid mechanics. The technique holds the potential of considerably simplifying the inclusion of chemistry in the computation of

high speed fluid flows.

The proposed minimum budget will simply continue, at a somewhat reduced level, the current activities. It is hoped that a possible return to the original proposed funding will permit enhancement of activities which we believe will strengthen the Center. First is a proposed expansion of the number of faculty involved and the second is a significant effort to specifically recruit some of the best students into the Center's activities via a "Center Fellowship" program. The planned long-term visits of Prof. Claudio Bruno will be primarily concerned with Prof. Jameson, but will have considerable interactions with Prof. Glassman and Prof. Lam. This visit should provide a major focal point for more detailed visits to Princeton by NASA personnel and Prof. Bruno spending some time at NASA-Langley. The proposed long-term visits of NASA staff at Princeton, to be involved in both research and teaching, will provide us with our first experience in that area.

Appendix 1:

Princeton University
Center for High Speed Gas Dynamics
Lecture Series

1989

- | | | |
|----------|--|----------------------------------|
| March 27 | Richard D. Neumann | Wright Field Flight Dynamics Lab |
| | “The Use of Experimentation in the Age of Computations” | |
| March 29 | Richard D. Neumann | Wright Field Flight Dynamics Lab |
| | “The Enabling Technology for Ground and Flight Test” | |
| April 10 | Robert Cattolica | Sandia National Labs |
| | “Laser-Fluorescence Measurements of Nitric Oxide in
Hydrogen/Oxygen Flames” | |
| April 12 | Robert Cattolica | Sandia National Labs |
| | “Advanced Optical Diagnostics for Hypersonic Research” | |
| May 1 | Donald Baganoff | Stanford University |
| | “Direct Numerical Simulation of Low Density Hypersonic Flows” | |
| May 2 | Donald Baganoff | Stanford University |
| | “Research Problems Associated with the Application of Particle
Methods to the Study of Rarefied Hypersonic Flows” | |
| May 9 | Seymour M. Bogdonoff | Princeton University |
| | “Hypersonics - The Testing Dilemma” | |
| May 16 | Sin-I. Cheng | Princeton University |
| | “Hypersonic Propulsion & Turbulent Combustion” | |
| July 7 | Robert W. Bilger | University of Sydney |
| | “New Results for Structure and Theory of Turbulent Flames” | |

October 24	Dean Chapman	Stanford University	
			“High-Altitude Hypersonic CFD for the Continuum Transitional Regime”
Nov. 8	Shigeo Kida	Princeton University	
			“Numerical Studies of Incompressible & Compressible Turbulence”
			(Canceled)
Nov. 13	Ken Stetson	Wright Patterson AFB, Ohio	
			“Hypersonic Boundary-Layer Transition - Part One”
Nov. 14	Ken Stetson	Wright Patterson AFB, Ohio	
			“Hypersonic Boundary-Layer Transition - Part Two”
Nov. 17	Eric Jumper	Notre Dame	
			“Oxygen Recombination on Space Shuttle, Thermal-Protection-Tile-Like Surfaces”
Nov. 21	Claudio Bruno	University of Rome	
			“Gas/Surface Interaction and Thermal Load Modeling in Hypersonic Flow”
1990			
Feb. 20	Seymour M. Bogdonoff	Princeton University	
			“Modeling of Three-Dimensional Shock-Wave/Turbulent Boundary Layer Interactions”
Oct. 18	Phillipe Poisson-Quinton	ONERA	
			“The Future of High Speed Transportation After Concorde”
Oct. 19	Phillipe Poisson-Quinton	ONERA	
			“Aeronautical Research as Seen from Europe”

Appendix 2:

Trip Report

Dr. Claudio Bruno

PRINCETON UNIVERSITY: Center for High Speed Gas Dynamics

November 21, 1989

TO: Professor Seymour M. Bogdonoff
Director, Center for High Speed Gas Dynamics

FROM: Dr. Claudio Bruno

SUBJECT: Trip Report

What follows is a succinct account of the meetings and discussions I had with people working in the hypersonics area, and of ideas and suggestions that could be potentially useful to NASA.

1. Professor Eric Jumper, University of Notre Dame, (219) 239-7680. Works in O, N recombination over SiO₂, SiN surfaces. Has talked with Carl Scott, NASA-Johnson, about his and my theory (presence of metal impurities causing recombination for Shuttle RCG TPS). Told me Carl is beginning to pay attention to metal theory. Has Shuttle tile, useable to do simple experiments, to check also γ , β (accommodation factor) for $O \rightarrow O_2$. Propose to meet here, November 17th to discuss common interests.
2. Harvey Lam. Explained to him my model for surface NO formation. Agrees that detecting it would imply measuring vibrational excitation of desorbing NO (as opposed to gas-phase formed NO). Mentioned to him industrial plasma torch applications. Harvey thinks the major unknown is electronic de-excitation occurring at surface (e.g., $Ar^+ + e^- \rightarrow Ar$).
3. Alex Harris, Bell Labs, (201) 582-6522. Gave lecture in Frick on measuring vibrationally excited surface molecules. He excites them with a laser, measures relaxation times (related to β). Told me O₂, N₂ are poor gas-phase vibrators,

excellent chemisorbed vibrators. His work has just started. Advises talking with Steve Bernasek (Frick).

To check NO surface formation, advises classical experiment with 2 N₂, O₂ beams impinging on metal or TPS surface. If NO is formed, detection would be via IR adsorption or laser beam scattering. Thus, feasible. Useful for both SCRJ and external aerodynamics people at NASA.

4. Professor Graham Candler, North Carolina State University, (919)737-2365. The paper he presented at the AIAA Thermophysics conference in Buffalo is consistent with the 'bimodal' Vibr. distribution claimed by C. Park and coworkers at Ames. However: recent findings (Ho, Ames, whom I saw in June; Hassan) point to rotational nonequilibrium as a player in causing V energy to be transferred to Translational mode. It is possible that the dreaded 'vibrational bottleneck' may be less important than previously thought. If true, TPS for AOTV and Titan probe may work under conditions closer to equilibrium than assumed in Park's calculations. Strong implications for NASA. Candler is working at reducing the VV & VT scheme for N₂. There are 56 VV rate equations for N₂, and almost the same number for O₂. I suggested to him Peters' and Lam CSP techniques. Sent him relevant papers. I mentioned Peter Gnoffo is already working with Lam at Langley.

5. Professor Steve Bernasek, Frick Lab (x8-4986). Does work on vibrationally excited species desorption. Mentioned work done by Cavanaugh, Stevenson at NBS is measuring vibrational relaxation of NO, CO, NH₃ species from SiO₂ and Al₂O₃. Times are ~ 100 picoseconds, implying $\beta \simeq 1.0$. Said that electron beams can be used for N₂ excitations. He could measure vibrational temperatures in excited O₂, N₂, H₂, and has to do this in near vacuum. Could duplicate Rosner's work in the '70s. Said that NO vibrational relaxation is easier to

measure than either O_2 or N_2 . Notes that for very high T viscous layers radiation from gas may influence surface chemistry.

Measurements done together with Steve could be very useful for both the excited species desorption and the surface NO questions. He is interested in finding ways of collaborating and doing work for NASA.

6. Professor Sigurd Wagner, EE SS. I asked him about measuring the % of crystal SiO_2 on RCG. He said X-ray diffraction (XRD), that works well for layers thicker than $1\ \mu m$, would be the technique of choice. Raman laser scattering also useable. XRD is standard, and could be done in the chemistry department. This could assess the effect of exposure of RCG to repeated re-entry T cycles, and then one could correlate that with increases in reactivity, of concern to the TPS division at Ames.
7. Professor Irv Glassman. Mainly interested in SCRJ research. He's attacking the parallel H_2/O mixing problem a) measuring ignition delay times and b) beginning to analyze the effect of pirophorics (such as fine Al powder) on shear layer stability. Following this conversation, I did a preliminary estimate of energy release effects vs. turbulent kinetic energy. A 0-th order estimate looks promising in terms of amount of Al powder needed. Next step I suggested is finding estimates for the extra turbulent KE created by the Al microexplosions. Both Irv and Ken Brezinsky like the idea. Agree to keep in touch. Gave Ken info on whom and how to contact at WPAFB for sponsoring purposes. I think that for parallel mixing this idea could be potentially very useful to the SCRJ group at Langley.
8. Dick Miles. Uses UV flashes through O_2/H_2 parallel streams to dissociate O_2 . Concept similar to Glassman's. Could

measure O_2 vibrational relaxation easily. NO would be tougher (its relax times are 3 times shorter).

Mentioned the vibrational 'scavenging' effect of H_2O . This could have a strong impact on a SCRJ wall HT, as the vibrationally excited species desorbing could relax close to the wall due to H_2O presence, and increase HT. This could be of importance for the SCRJ people at Langley considering transpiration cooling.

9. Dr. Luigi Martinelli. Explained the code development work done in Jameson's group. Work is limited to low supersonic. Thinks switching to hypersonics could pose serious computational problems due to scarce knowledge of transition near nose. DNS accuracy poor, for low order (<6) techniques. I mentioned my interest in formulating constitutive equations for turbulent compressible flows, in collaboration with R. Borghi in France. We'll keep in touch about these.
10. Professor Antony Jameson. Still considering whether to do hypersonic calculations. Would prefer to stay away from real gas effects.
11. Dr. Carl Scott, NASA-Johnson. Told me about the RCG coating developed at Ames and its rationale. Told me to talk to David Stewart, at Ames. Is considering giving a contract to Chemical Dynamics Corporation to measure surface structure and, later, β and γ on polycrystalline SiO_2 . Was not aware of the OH-Si bond presence on amorphous SiO_2 , that could have a large impact on reactivity. I suggested investigating this. Will let me know.
12. Ken Stetson, WPAFB. Asked him about turbulent KE measurements in the transition region (none). I suggested looking at effect of heating/cooling on BL transition due to 2nd mode.

13. David Stewart, NASA-Ames, (415) 694-6614. Responsible for most of the development of RCG coating on Shuttle. Gave me a good account of rationale for choice of material. XRD done to post-flight tiles, claims no OH detected. Thinks reactivity increases with time due to exposure to salty air. Did not know of preferential sodium attack of amorphous vs. crystalline SiO_2 . Gave me data on AFE. We agreed on catalytic recombination effects for AOTV (some people, instead, think them unimportant, due to large size).
14. Harvey Lam. Went to see him re: CSP technique. Told me of Gnoffo's application. I told him about Candler problem and how CSP could be applied to solve it.
15. Eric Jumper, Univ of Notre Dame. After seminar, discussed possible experiments to propose to NASA-Johnson. Told me Scott has some discretionary money he could give him immediately. Asked me for advice on experiments. In view of Scott interest for metal effects on TPS, I suggested simple metal detection experiments on the tile he has; also, detection of O_2 delta singlet as an excited species (preferential mode of excited O_2 desorption). We'll keep in close touch. Possible interaction with Steve Bernasek, whom we visited.
16. Sin-I Cheng. Discussed some items in his Hypersonic Propulsion paper. I suggested O, NO from shock and/or inlet surface could be made to be ingested by combustor. Impact on combustion, potentially very attractive. He disagrees to some extent on whether this could be practicable. We agree on using catalytically-coated surfaces for reducing i.d. time, and also to increase recombination in nozzle. I suggested some changes to paragraph of his paper dealing with his H_2/O_2 surface combustion concept.

Appendix 3:

Report by Glassman et al.

A NEW DEFINITION AND THEORY OF METAL PYROPHORICITY

BY

I. Glassman, P. Papas and K. Brezinsky
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Interest in the use of pyrophoric metals to initiate combustion and to increase mixing and recombination of radicals in supersonic combustion engines has led to a more thorough consideration as to what pyrophoricity really is and to develop a model that would permit the calculation of the particle size that can be pyrophoric.

There have been many (1,2,3) descriptions of pyrophoricity, but no truly precise definition. Dictionaries define pyrophoricity as the capability of igniting spontaneously in air. Silane gas spontaneously ignites on contact with air and is thus termed pyrophoric. In rocket combustion hypergolicity is termed the spontaneous ignition upon contact with a complementary substance. To be proposed is a definition of pyrophoricity which pertains solely to condensed phases such as metals, semiconductors, etc. Thus it is proposed that silane gas be considered hypergolic with air. Also, zirconium is thought to be pyrophoric, but by the definition to be proposed is not.

Metal dust clouds can explode, but more exactly propagate a deflagration or detonation. Metal particles which explode are not pyrophoric or they could not exist in a cloud without spontaneous consumption. Indeed finely divided metal particles which have a protective oxide coat and are dispersed in air can propagate a combustion wave. In this case some ignition or thermal source destroys the protective oxide of a group of particles, causes the remaining metal to react and releases sufficient heat to destroy the protective coats of nearby particles and so on, so a flame and then possibly a detonation can generate. This perception of propagation holds for any dust cloud of combustible material such as an agricultural powder.

It is suggested that the term pyrophoricity should pertain to the instantaneous combustibility of fine metal particles which have no oxide coat. Thus what determines whether a metal will be pyrophoric are primarily its particle size, a measure of its surface area to volume ratio, and its thermochemical properties. Due to heat losses during the initial oxidation process, very small, uncoated metal particles may, or may not, be pyrophoric. Pyrophoricity, as explosivity, must pertain to a cloud of particles.

Thus, it is proposed that a metal be considered pyrophoric when in its nascent state (no oxide surface coating) it is small enough that the initial oxide coat that forms due to heterogeneous reaction with air under ambient conditions generates sufficient heat to vaporize the remaining metal. Metal vapors thus exposed are extremely reactive with oxidizing media and are consumed very rapidly.

In earlier work related to solid propellant rocketry, the senior author (4) established a criterion for vapor phase combustion of metals. Noting that the flame temperature of a metal was limited to the boiling point of its oxide and that, during vapor phase combustion of condensed phase particles, the particle rapidly achieves a temperature close to, but always a little below, its boiling point, he postulated that for a metal particle to undergo vapor phase combustion the boiling point of the metal oxide must be greater than the boiling point of the metal, i.e., the temperature created by the oxidation process must be

sufficient to vaporize the metal. When the contra condition was true, that is the metal boiling point was greater than the oxide, then the metal could only undergo a slow heterogeneous surface reaction and if the surface oxide coat retained its integrity that the metal consumption could be very slow and could indeed even stop. Examination of available thermophysical properties would indicate that B, Si, Ti, Cu, Fe, and Zr can only be consumed by oxidation through heterogeneous surface reaction; that is, they cannot undergo vapor phase combustion. By the postulated definition of pyrophoricity, these metals cannot be pyrophoric. As stated earlier, fine particle clouds can be explosive. Thus as Dahn (1) states, Zr clouds can be highly explosive, however the authors of this paper claim Zr is not pyrophoric. Why Zr is considered "highly explosive" will be discussed subsequently.

By the definition proposed it becomes possible to estimate the sizes of metal particles in their nascent state that will be pyrophoric. This estimate is achieved by a calculation that appears very simple when reasonable assumptions are made. First the problem is considered to be time independent. Physically this assumption is realistic because the particle sizes are very small and the thermal conductivities of the metallic fuels are large. Second, no heat losses from the particles are assumed. The largest loss would be by radiation, but in a particle cloud a single particle "sees" particles of the same temperature. The oxide thickness assumed to form initially and to vaporize the remaining metal is that of the limiting techniques at room temperature reported in the literature. Lastly, it has been assumed that the densities of the metal and the oxide could be taken as those at room temperature. Since the proposed analysis is on a mass basis and it is initial particle size that is desired, the density assumption is more than adequate.

Although pyrophoric metals can come in various shapes, solid spheres, porous balls or flakes, the calculation will be based on spherical metal particles. Since it is the surface area to volume ratio that determines the critical condition, then it would be obvious for a particular metal flake which would be pyrophoric could have smaller mass than a sphere of the same metal. However, due to surface tension, pyrophoric flakes will become spheres as the metal melts.

If r is assumed to be the radius of the metal particle with its newly formed oxide coat and δ the thickness of the oxide coat, then the critical heat balance for pyrophoricity is

$$\begin{aligned} \frac{4}{3} \pi \left\{ r^3 - (r-\delta)^3 \right\} \rho_{\text{ox}} (-\Delta H_{298}^{\circ})_{\text{ox}} - \frac{4}{3} \pi (r-\delta)^3 \rho_m \left\{ (H_{T_v}^{\circ} - H_{298}^{\circ}) + L_v \right\}_m \\ + \frac{4}{3} \pi \left\{ r^3 - (r-\delta)^3 \right\} \rho_{\text{ox}} \left\{ H_{T_v}^{\circ} - H_{298}^{\circ} \right\}_{\text{ox}} \end{aligned} \quad (1)$$

where $(\Delta H_{298}^{\circ})_{\text{ox}}$ is the standard state heat of formation of the oxide at 298K, H_T° is the standard state enthalpy at T , T_v specifies the metal vaporization temperature, and the subscripts m and ox refer to the metal and oxide respectively.

Equation 1 can be simplified and rearranged to give the form

$$\begin{aligned} [\rho \{ (-\Delta H_{298}^{\circ}) - (H_{T_v}^{\circ} - H_{298}^{\circ}) \}]_{\text{ox}} / [\rho \{ (H_{T_v}^{\circ} - H_{298}^{\circ}) + L_v \}]_m = \\ (1 - (\delta/r))^3 / [1 - (1 - (\delta/r))^3] \end{aligned} \quad (2)$$

Considering the r.h.s. of Eqn. 2 as a simple mathematical function, it can be plotted versus (δ/r) . The l.h.s. of Eqn. 2 is a known for a given metal; it contains known thermochemical and thermophysical properties, thus (δ/r) is determined. Since the original oxide thicknesses δ is estimated from the literature, r can be determined. The mass of oxide initially formed is greater than the mass of metal consumed, consequently the original size of the metal that would be pyrophoric (r_m) can be calculated from δ , r and the physical properties of the oxide and metal and their molecular weights.

Figure 1 is a functional form of the r.h.s. of Eqn. 2. Since the ordinate values for a metal can be determined, the position of various metals can be placed on the curve defining the function given by Eqn. 2. The smaller the (δ/r) the greater is the pyrophoric tendency of the metal. Because there are not large variations in δ , when (δ/r) is large, then to be pyrophoric the r_m must be very, very small. Quite importantly, it should be noted that it is not likely that metals which have values of (δ/r) much larger than 0.2 can be made small enough in size to be pyrophoric.

The pyrophoric particle size of many metals has been calculated. Table 1 lists the calculated results of some metals where experimental values of δ and $2 r_{exp}$ are reported in the literature. For the few experimental values of $2 r_{exp}$ found the agreement with the calculated values based on the proposed steady state analysis is quite good. The agreement with U and Zr is not, but the authors claim that U and Zr cannot be pyrophoric in that they do not follow Glassman's criterion (4) for vapor phase combustion - the oxide cannot release enough heat to vaporize the metal. These metals appear pyrophoric because the oxide coats which formed when the nascent metals are exposed to the oxidizer releases enough heat so that at a given developed temperature the oxides continually form crevices that permit the oxidizer to penetrate to the bare metal surface and consume the metal. Though this process releases a great deal of heat, it is slow. A true pyrophoric metal such as Al is essentially consumed instantaneously when exposed to the oxidizer. Similarly the agreement between the calculated and experimental values of Cu and Fe may be fortuitous. Fe scales (rusts) at room temperatures and Cu forms a powdery oxide at higher temperatures. Thus their fate is the same as U and Zr.

Kubachewski and Hopkins (5) report that ZrO_2 essentially becomes non protective at about 1200 K. One can apply Eqn. 2 and determine what oxide thickness would be required to raise the metal and oxide formed to 1200 K and thus start relatively rapid surface oxidation. For the experimental value $2r_m = 3.0 \mu m$, δ equals 224 Å, which appears quite reasonable considering the range of values of δ reported as a function of temperature (Polling and Charlesby (6)). Similarly, it is reported that there is serious scaling of UO_2 at about 525K. If $10 \mu m$ is the current value for the U size for rapid combustion, according to the analysis proposed, δ would be 209 Å - also very reasonable.

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Table 1

Comparison of Experiment and Theory - Metal Pyrophoricity

Metal	Oxide	δ/r	δ/r_m	$\delta, \text{\AA}$	$r, \mu\text{m}$	$r_m, \mu\text{m}$	$2r_m, \mu\text{m}$	$2r_{\text{exp}}, \mu\text{m}$
Al	Al_2O_3	0.175	0.183	25	0.0143	0.0137	0.0273	0.03
Cu	CuO	0.821	0.994	45	0.0054	0.0045	0.0091	0.01-0.03
Fe	FeO	0.582	0.691	35	0.0060	0.0051	0.0101	0.01-0.03
Pb	PbO	0.372	0.396	31	0.0083	0.0078	0.0157	0.01-0.03
U	UO_2	0.327	0.376	25*	0.0076	0.0066	0.0133	10
Zr	ZrO_2	0.285	0.309	50	0.0175	0.0162	0.0324	3.0

* estimate

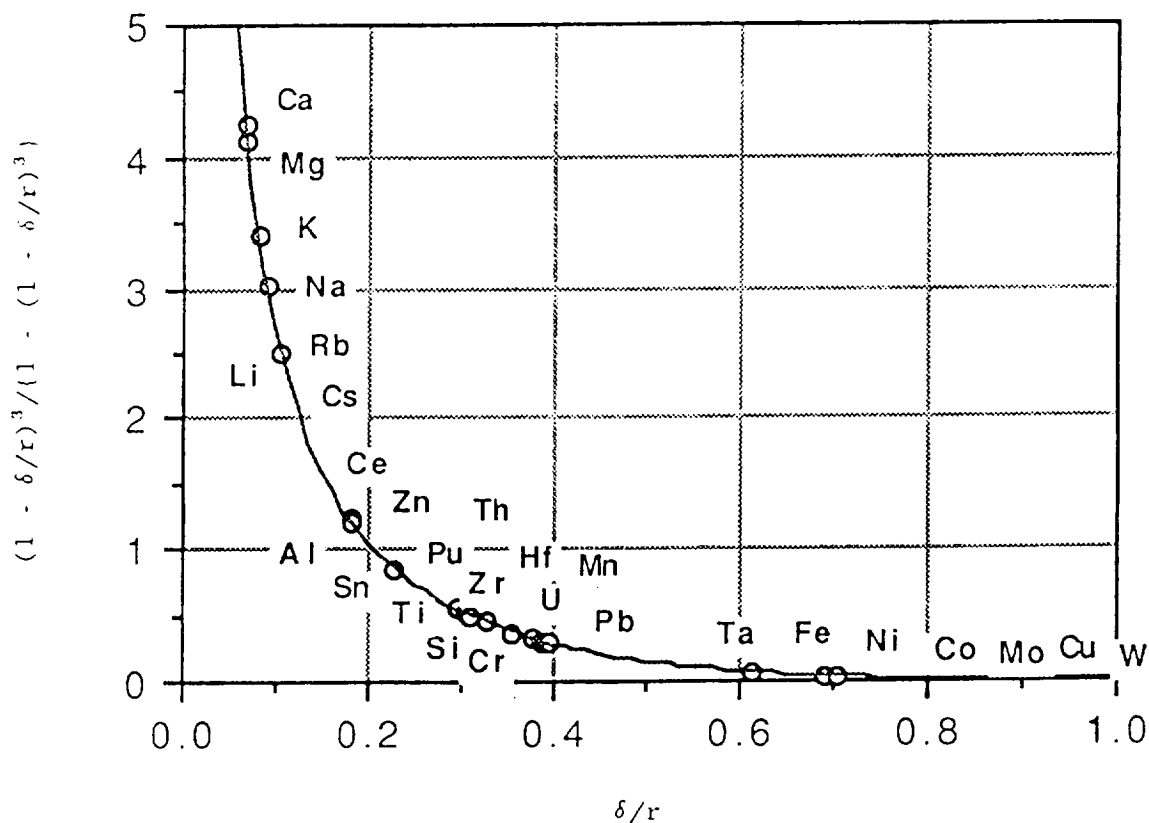


Figure 1. The Pyrophoricity Function for Various Elements